TRANSFER OF VOLATILE COMPOUNDS FROM SOIL: COMPARISON BETWEEN PREDICTIONS AND FIELD MEASUREMENTS WITH DIFFERENT MODELS; DEVELOPMENT OF THE VOLASOIL MODEL FOR A DEPLETING SOURCE

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Key words: contaminated soil, vapour, indoor air, transfer, model, measure, finite source, attenuation.

1. Summary

Soil vapour migration into buildings, and subsequent inhalation, are often the main exposure pathway to humans at sites contaminated with Volatile Organic Compounds (VOCs). For such sites, the quantification of pollutant concentrations in the indoor air is essential while assessing risks for the human health. Modeling is often necessary, for example in the view of future situations, but also in combination with site measurements.
The Johnson & Ettinger and VOLASOIL models are the two models mainly used in Europe to predict indoor air concentrations.
The validation of these models is still incomplete, beyond some global verification of indoor air concentrations: step by step measurements for a detailed model calibration and "validation" hardly exist in the literature, and predictions of indoor air concentrations from different models sometimes vary by several orders of magnitude. Verifying and improving vapour intrusion models is necessary for a better risk estimation and subsequent site management.
Besides, the VOLASOIL model does not represent the depletion of the source due to the volatilization, beyond an overall mass control; this may result in over-conservative estimates of indoor air concentrations, for example when a VOC source is near the soil surface.

This paper first presents a development of the VOLASOIL model (in its multilayer version) for a depleting source with a site application, and secondly two site studies where detailed site "validation" data were collected and compared to model results.

The site investigations (2003-2006) concerned the pollutant concentrations in soil, soil gas, indoor air, and pollutant flux at the slab surface, and key model parameters: depth of the pollution, characteristics of the soil and of the building (slab, atmospheric / soil pressure difference, ventilation rates…). They were conducted at different seasons.
The transfer modeling, from soil and soil gas to indoor air, was performed with two transport models, based on the equations respectively of Johnson & Ettinger, and of VOLASOIL (multilayer version). A comprehensive sensitivity analysis was undertaken.

The modeling of a depleting source led to downsize the vapour flux by one order of magnitude or more over one year at the application site. This illustrates the interest of this modeling. The mathematical developments of VOLASOIL presented here should allow a broader use of VOLASOIL, *e.g.* for a building with a concrete slab.
The comparisons between predicted and measured concentrations in indoor air showed on the real site over-prediction and in some cases under-predictions of the models by one or two orders of magnitude. In spite of an extensive site characterisation, those differences, and the significant time and space variability in measured soil gas or indoor air concentrations could often not be explained. Significant impacts on the

modelled concentrations could be obtained by modifying the parameter values within their respective possible ranges.

The study emphasizes the importance of a humble attitude towards the results of the modeling of vapour transfer, in the current state of model validation. Combining models and measurements is essential for a "robust" risk assessment. A comprehensive understanding of the model used, its concept and its equations, is essential. We recommend to re-code one's own tools so as to better test and understand the sensitivity of the model in different situations.
Improvements in modeling and measuring vapour intrusion are still possible. When dealing with finite source modelling, the research should be extended to the impact of degradation in the vadose zone for benzene and e.g vinyl chloride as a source of variability and systematic differences. Detailed quantitative measurements and interpretation of the main site parameters appear essential when aiming at model verification.
This is a difficult and time-consuming work, which has to be repeated with different types of sites (building designs, construction materials, soil) and at different periods under adequate conditions (heating, "normal" ventilation…). Collaborations are needed, at national and international scales, so as to gather strengths on data collection and interpretation. Such collaborations are initiated for example with the HERACLES initiative and with the French and European research projects FLUXOBAT and CITYCHLOR about chlorinated solvents pollution in soil and groundwater.

2. Introduction

Soil vapour migration into buildings, and subsequent inhalation, are often the main exposure pathway to humans at sites contaminated with Volatile Organic Compounds (VOCs). For such sites, the quantification of pollutant concentrations in the indoor air is essential while assessing risks for the human health. Modeling is often necessary, for example in the view of future situations, but also in combination with site measurements: both modeling and measuring present important uncertainties, their combination helps reaching a more "robust" site assessment.
A variety of soil vapour intrusion algorithms, or « empirical » / dilution factors are available that calculate transfer of soil gas to the indoor air (not exhaustive list [1 to 11, 22, 23]). The Johnson & Ettinger and VOLASOIL models are the two models mainly used in Europe.

The validation of these models is still incomplete, beyond global verification of predicted indoor air concentrations and comparisons of model results in different situations [e.g. 23]: step by step measurements for a detailed model calibration and "validation" hardly exist in the literature, and predictions of indoor air concentrations from different models sometimes vary by several orders of magnitude. Verifying and improving vapour intrusion models is necessary for a better risk estimation and subsequent site management.
Besides, the VOLASOIL model does not represent the depletion of the source due to the volatilization, beyond an overall mass control; this may result in over-conservative estimates of indoor air concentrations, for example when a VOC source is near the soil surface.

This paper first presents a development of the VOLASOIL model (in its multilayer version) for a depleting (finite) source with a site application, and secondly a site study where detailed site "validation" data were collected and compared to model results.

The site investigations (2003-2006) concerned the pollutant concentrations in soil, soil gas, indoor air, and pollutant flux at the slab surface, and key model parameters: depth of the pollution, characteristics of the soil and of the building (slab, atmospheric / soil pressure difference, ventilation rates…). They were conducted at different seasons. Following previous works presented at CONSOIL 2003 [16] and 2005 [10] (site n^r 1), the site study included a new site (site n^r 2) and new compounds (BTEX and naphthalene beside chlorinated solvents).

The transfer modeling, from soil and soil gas to indoor air, was performed with two transport models, based on the equations respectively of Johnson & Ettinger [4], and of VOLASOIL (multilayer version, [10], [20]). A comprehensive sensitivity analysis was undertaken.

The goal of this research is to help improve the site-specific selection and application of vapour transfer models, for better risk-based actions (remediation, action on current buildings or future construction plans,…).

3. Development of the VOLASOIL model for a depleting source

3.1. Conceptual model

We consider here n successive layers of homogeneous material (soil or concrete) in the vadose zone (Figure 1), indexed from the polluted layer (i=0) up to the surface (i=n for the layer in contact with the indoor air: crawl space, basement, or first floor).

The flux mechanisms supposed to occur are the diffusion in the soil water and in the soil gas, and the convection in the soil gas. Besides, the multiphase equilibrium between soil gas, soil water, and soil, is considered to take place (right side of Figure 1). The different fluxes are not independent: it is the same soil gas (or soil water in equilibrium with the soil gas) which is simultaneously submitted to the different mechanisms.

The conceptual model developed here for the depletion of the source is a progressive descent of the top of the source with time, as it looses its pollution through volatilisation.

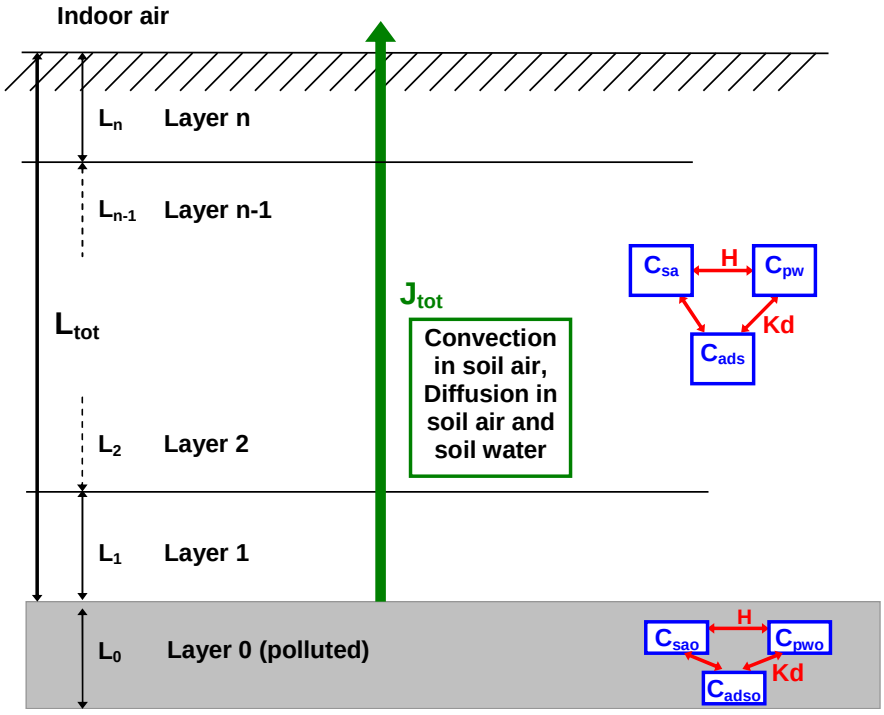

Figure 1: Multilayer model of vapour intrusion (see § 3.2 for parameter definition)

3.2. Steady-state model for a multilayer soil

Hazebrouck *et al*. (2005, [10]) established the equation of the total pollutant flux J_{tot} [mg/m^2/s] which combines the convection and the diffusion (here neglecting the indoor air concentration), as in the new version of VOLASOIL [20][1]:

[1] A further development integrating the evapotranspiration water flux and the transfer within the capillary fringe and the groundwater is also available [4].

Equation 1 $$J_{tot} = \frac{F_{ci}}{1 - \exp\left(-F_{ci}\frac{L_{tot}}{DU_{tot}}\right)} Csa_o$$, with:

Equation 2 $$F_{ci} = 10^3 K_{tot} \frac{\Delta P_{is}}{L_{tot}}$$;

$$L_{tot} = \sum_{i=1}^{n} L_i \; ; \; \frac{L_{tot}}{K_{tot}} = \sum_{i=1}^{n} \frac{L_i}{K_i} \; ; \; \frac{L_{tot}}{DU_{tot}} = \sum_{i} \frac{L_i}{DUa_i}$$;

Equation 3 $DUa_i = D_{swi} / H + D_{sai}$, and:

Parameter	Symbol	Unit
Convective flux of soil gas into the building	F_{ci}	$L/m^2/s$
Soil gas concentration in the source (layer 0 or L_0)	Csa_o	mg/L_{sa}
Total depth of the source, or thickness of material above the pollution	L_{tot}	m
Thickness of the layer i	L_i	m
Air-conductivity of the layer i	K_i	$m^3/m/Pa/s$
Mean air-conductivity of the vadose zone (soil + floor) above the pollution	K_{tot}	$m^3/m/Pa/s$
Pressure difference between the indoor air and the soil gas	ΔP_{is}	Pa
Mean multiphase diffusion coefficient on the n layers expressed from the soil gas concentration (diffusion in soil water and soil gas)	DU_{tot}	$(mg/m^2/s)/(mg/L_{sa}/m)$
Multiphase effective local diffusion coefficient in soil expressed from the soil gas concentration, in layer i	DUa_i	$(mg/m^2/s)/(mg/L_{sa}/m)$
Effective local diffusion coefficients in soil water / soil gas, in layer i (see Milligton-Quirk equations in Waitz *et al*, 1996)	D_{pwi}, D_{sai}	$(mg/m^2/s)/(mg/L_{(pw/sa)}/m)$
Air / water partitioning coefficient (Henry coefficient)	H	$(mg/L_a)/(mg/L_w)$

3.3. Numerical conservative solution for a depleting source, taking into account both convection and diffusion

We consider here a progressive descent of the top of the source, starting from the depth Ltot at t=0, down to a depth $L_{tot}(t) = L_{tot} + z_o(t)$ at time t, where $z_0(t)$ is the "cleaned" thickness in the source layer L_0. The soil gas flux F_{ci} from the top of the source to the indoor air, the mean multilayer and multiphase diffusion coefficient DUa, are now also time-dependent (they decrease with time).

The flux of VOC carried out, in mg/m^2, between time t_0=0 and time t is :

Equation 4 $$Q_{out}(t) = \int_0^t J_{tot}(y)\,dy ,$$

By mass conservation, this flux is connected to the "cleaned" thickness $z_0(t)$ in the source layer L_0:

Equation 5 $$Q_{out}(t) = 10^3 \, SD \, C_s \left[z_0(t) - z_0(t=0)\right]$$

and the soil concentration C_s in the source layer is connected to the soil gas concentration Csa_0 :

Equation 6 $$CT_{s\to sa} = Csa_o / C_s = \frac{H}{Kd + Vw/SD + H\,Va/SD}$$, with :

Parameter	Symbol	Unit
Volumic fraction of water/air in the soil (here in the source layer)	Vw/Va	l_{pw}/l_{soil} and l_{sa}/l_{soil}
Dry soil bulk density	SD	kg_{dm}/l_{soil}
Soil water partitioning coefficient (here in the source layer)	Kd	$(mg/kg_{dm})/(mg/l_w)$
Total mass concentration of pollutant in the soil (reported to dry soil) (here in the source layer)	Cs	mg/kg_{dm}
Soil / soil-air partitioning coefficient (here in the source layer)	$CT_{s\to sa}$	$(mg/l_{sa})/(mg/kg_{ms})$

Combining equation 4 and equation 5, we obtain :

Equation 7 $$10^3\ SD\ C_s\ z_o'(t) = J_{tot}(t) = \frac{F_{ci}(t)}{1 - \exp\left(-F_{ci}(t)\frac{L_{tot}(t)}{DU_{tot}(t)}\right)} Csa_o$$

Using $L_{tot}(t) = L_{tot} + z_o(t)$, and then: $\frac{L_{tot}(t)}{K_{tot}(t)} = \frac{L_{tot}}{K_{tot}} + \frac{z_o(t)}{K_o}$ and $\frac{L_{tot}(t)}{DU_{tot}(t)} = \frac{L_{tot}}{DU_{tot}} + \frac{z_o(t)}{DU_o}$, and with the expression of $F_{ci}(t)$ given in Equation 2, Equation 7 becomes a differential equation with no analytical solution (to our knowledge).

An analytical solution is reachable when we use the (slightly over-)conservative[2] estimate of the total flux $J_{tot}(t)$ as the addition of two independent fluxes:

- The pollutant flux due to convection alone: $J_{conv}(t) = Csa_o\ F_{ci}(t) = Csa_o 10^3\ \Delta P_{is} \frac{K_{tot}(t)}{L_{tot}(t)}$, and
- The pollutant flux due to diffusion alone: $J_{diff}(t) = DU_{tot}(t)\frac{Csa_o - Csa_n}{L_{tot}(t)} = DU_{tot}(t)\frac{Csa_o}{L_{tot}(t)}$

Then Equation 7 becomes :

Equation 8 $$10^3\ SD\ C_s\ z_o'(t) = \frac{Csa_o\ 10^3\ \Delta P_{is}\ K_o\ K_{tot}}{K_o\ L_{tot} + K_{tot}\ z_o(t)} + \frac{Csa_o\ DU_o\ DU_{tot}}{DU_o\ L_{tot} + DU_{tot}\ z_o(t)}$$ or

Equation 9 $$\frac{CT_{s\to sa}}{10^3\ SD} = \frac{a\ z_o^2(t) + b\ z_o(t) + c}{d\ z_o(t) + e} z_o'(t) = \left[\alpha\ z_o(t) + \beta + \frac{\gamma}{d\ z_o(t) + e}\right] z_o'(t)$$

with the following definitions:

$a = DU_{tot}\ K_{tot}$ $b = L_{tot}\ (K_o\ DU_{tot} + K_{tot}\ DU_o)$ $c = DU_o\ K_o\ L_{tot}^2$ $d = K_{tot}\ DU_{tot}\ (10^3\ \Delta P_{is}\ K_o + DU_o)$

$e = K_o\ DU_o\ L_{tot}\ (10^3\ \Delta P_{is}\ K_{tot} + DU_{tot})$ $\alpha = a/d$ $\beta = (b - a\ e/d)/d$ $\gamma = c - \frac{e}{d}\left(b - \frac{a\ e}{d}\right)$

The solution of the differential equation 9 can be expressed as:

Equation 10 $$z_o(t) = G^{-1}\left[G(z_o(t=0)) + \frac{CT_{s\to sa}}{10^3\ SD}\ t\right]$$

where the function G(x) is defined as following:

Equation 11 $$G(x) = \frac{\alpha}{2}x^2 + \beta\ x + \frac{\gamma}{d}\ln\left(x + \frac{e}{d}\right)$$.

There is no <u>analytical solution for $z_o(t)$ but it can be determined numerically</u> by finding a root to the following equation:

Equation 12 $$G[z_o(t)] - G[z_o(t=0)] - \frac{CT_{s\to sa}}{10^3\ SD}\ t = 0$$.

With the numerical solution of $z_o(t)$, the mean flux of VOC carried out, in mg/m^2/s, over the period of time t can be deduced from equation 5:

Equation 13 $$\frac{Q_{out}(t)}{t} = 10^3\ SD\ C_s\ \frac{\min\{L_o\ ;\ z_0(t) - z_0(t=0)\}}{t}$$,

where the depletion of the source is limited to the thickness L_o of the contaminated layer.
The ratio between this mean flux of VOC and the concentration Csa_o in the soil gas at the source is then:

Equation 14 $$CT_{sao\to em} = \frac{Q_{out}(t)}{t\ Csa_o} = \frac{10^3\ SD}{CT_{s\to sa}}\ \frac{\min\{L_o\ ;\ z_0(t) - z_0(t=0)\}}{t}$$.

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[2] $J_{tot} < J_{conv} + J_{diff}$ [10]: the pollutant transfer caused by the combination of the convection and the diffusion is lower than the addition of the convection and the diffusion considered separately. The over-estimation is lower than a factor two, and particularly low when the convection is largely dominant over diffusion.

3.4. Analytical solution taking into account only the convection

As we could not get an analytical solution for the convection and diffusion equations together, we developed a VOLASOIL model for a finite source taking into account only the convection. In fact, a finite source modelling is needed only in cases of important fluxes, which are generally essentially convective. When using this modelling, it should then be checked after the modelling that the diffusion-alone flux remains low in comparison to the convective flux obtained (or, to be more surely conservative, it can be added to the only-convective flux obtained with depletion).

By taking into account only the convection, the equation 4 could be simplified :

Equation 15 $$Q_{out}(t) = \int_0^t J_{tot}(y)\,dy = \int_0^t J_{conv}(y)\,dy = \int_0^t Csa_o\, F_{ci}(y)\,dy = \int_0^t Csa_o 10^3\, \Delta P_{is} \frac{K_{tot}(y)}{L_{tot}(y)}\,dy$$

As equation 5 is still valid, equation 8 becomes :

Equation 16 $$10^3\, SD\, C_s\, z_o'(t) = \frac{Csa_o\, 10^3\, \Delta P_{is}\, K_o\, K_{tot}}{K_o\, L_{tot} + K_{tot}\, z_o(t)}$$ or

Equation 17 $$z_o'(t) = \frac{CT_{s\to sa}\, \Delta P_{is}}{SD} \frac{K_o}{K_o\, L_{tot}/K_{tot} + z_o(t)}$$

This differential equation can also be written :

Equation 18 $$d\left[\frac{K_o\, L_{tot}}{K_{tot}} + z_o(t)\right]^2 = \frac{2\,K_o\, CT_{s\to sa}\, \Delta P_{is}}{SD}\,dt$$

The solution of equation 18 is then:

Equation 19 $$z_o(t) = \sqrt{\frac{2\,K_0\, CT_{s\to sa}\, \Delta P_{is}}{SD}\ t + \left(z_o(t=0) + \frac{K_o\, L_{tot}}{K_{tot}}\right)^2} - \frac{K_o\, L_{tot}}{K_{tot}}$$

Equation 13 and Equation 14 are still valid, and the analytical solution of $z_o(t)$ can be used in it to determine mean flux of VOC carried out, in mg/m^2/s, over the period of time t.

If the pollution source occupies several soil layers, this solution can be applied successively to each of those layers, and the corresponding pollutant fluxes averaged over the total time. This requires the depletion time of each layer, which could be obtained by the numerical resolution of equation 19 with $z_0(t) = L_0$.

3.5. Application: modeled impact of the depletion

Method: A numerical application of the analytical solution was performed on a real case concerned with compounds ranging from less volatile (butanol, MethylEthylCetone) to more volatile (chlorinated solvents). We compared modeling results with depletion and without depletion in the hypothetical typical future conditions (closed and heated building). Indoor air measurements were also performed on the site but were not used (so far) for measure/model comparison. The conditions for that were not adequate: the building was largely open, the pressure difference between soil gas and indoor air was not measurable (< 1 Pa), and the source depletion would have been particularly slow to observe.

The soil consisted of two layers:

- A concrete slab with a thickness L_1 = 15 cm, and an air permeability K_1 = 1.1.10^{-6} m^2/Pa/s (medium quality: standard VOLASOIL value [8]).
- Filling material with an air permeability K_0 = 5.6.10^{-7} m^2/Pa/s, contaminated from the top at t = 0 (and as an exercise for some pollutants from a depth of 2.5 m; no down limit).

The exposure duration considered was 1 year, the lowest duration relevant for chronic risk estimate, corresponding to the ATSDR toxicological reference values (MRL: Minimal Risk Levels).

The compound parameters and the other soil parameters are reported in the following tables.

Parameter	Symbol	Unit	slab (medium quality)	Filling material
Organique carbone content	foc	%kgOC/kgms	0	3
Dry soil bulk density	SD	kgms/l	NC	1,5
Volumic fraction of water in the soil	Vw	lpw/lsol	0	0,15
Volumic fraction of air in the soil	Va	lsa/lsol	0,02	0,25

Parameter	Symbol	Unit	butanol	methylethyl cetone	vinyl chloride	cis-dichloroet hen	trichloroet hen	tetra chloro ethen	tetra chloro methan	trichloro methan
Molecular mass	M	(g/mol)	74,12	72,11	62,50	96,94	131,39	165,83	153,82	119,38
Diffusion coefficient in l'air	Da	(mg/m2/s)/(mg/l/m)	5,1E-3	5,3E-3	1,1E-2	7,4E-3	7,9E-3	7,2E-3	7,8E-3	1,0E-2
Diffusion coefficient in water	Dw	(mg/m2/s)/(mg/l/m)	5,1E-7	5,3E-7	1,2E-7	1,1E-6	9,1E-7	8,2E-7	8,8E-7	1,0E-6
Soil water partitioning coefficient	Koc	$(mg/kg_{OC})/(mg/lw)$	3,12	0,80	7,94	35,48	112,20	245,47	70,79	60,26
Henry Coefficient (15 - 20 ℃)	H	(mg/la)/(mg/lw)	3,59E -4	1,92E-3	1,12E+0	1,34E-1	4,28E-1	7,44E-1	8,90E-1	1,23E-1

Results: The transfer coefficients obtained are reported in the following table:

Parameter	Symbol	unit	butanol 0,15 m	butanol 2,65 m	methyléthylcetone 0,15 m	vinyl chloride 0,15 m	cis-dichloroethene 0,15 m	cis-dichloroethene 2,65 m	trichloroethene 0,15 m	trichloroethene 2,65 m	tetrachloroethene 0,15 m	tetrachloroethene 2,65 m	tetrachloromethan 0,15 m	trichloromethan 0,15 m	trichloromethan 2,65 m
No depletion of the source , diffusion only															
Total soil resistance to diffusion	L/Dueq	(mg/l)/(mg/m2/s)	5,4E+3	6,4E+3	5,2E+3	2,6E+3	3,8E+3	9,2E+3	3,5E+3	8,5E+3	3,8E+3	9,4E+3	3,5E+3	2,7E+3	6,5E+3
Transfer coefficient from soil air to surface-flux	CTsao->ém	(mg/m2/s)/(mg/l)	1,9E-4	1,6E-4	1,9E-4	3,8E-4	2,7E-4	1,1E-4	2,9E-4	1,2E-4	2,6E-4	1,1E-4	2,8E-4	3,8E-4	1,5E-4
With depletion of the source, diffusion and convection															
Total soil resistance to convection	L / Ktot	Pa.s/m	1,4E+5	4,6E+6	1,4E+5	1,4E+5	1,4E+5	4,6E+6	1,4E+5	4,6E+6	1,4E+5	4,6E+6	1,4E+5	1,4E+5	4,6E+6
Pressure difference indoor air / soil air	Δpis	Pa	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0	4,0E+0
Convective flux of soil air into the building	Fci	lsa / m2 / s	2,9E-2	8,6E-4	2,9E-2	2,9E-2	2,9E-2	8,6E-4	2,9E-2	8,6E-4	2,9E-2	8,6E-4	2,9E-2	2,9E-2	8,6E-4
CT from soil air to surface-flux	CTsao->ém	(mg/m2/s)/(mg/l)	2,9E-2	8,7E-4	2,9E-2	2,9E-2	2,9E-2	8,6E-4	2,9E-2	8,6E-4	2,9E-2	8,6E-4	2,9E-2	2,9E-2	8,7E-4
No depletion of the source, convection only															
Exposure duration (one year)	t	s	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7	3,2E+7
Air-conductivity source layer (filling)	K_0	m3/m/Pa/s	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7	5,6E-7
CT soil to soil air in the source layer	CTs-->sa	(mg/l d'air)/(mg/kg	1,9E-3	1,9E-3	1,6E-2	2,1E+0	1,1E-1	1,1E-1	1,2E-1	1,2E-1	9,8E-2	9,8E-2	3,8E-1	6,4E-2	6,4E-2
"Cleaned" thickness at t	$Z_0(t)$	m	3,5E-1	3,4E-2	1,1E+0	1,4E+1	3,2E+0	1,6E+0	3,3E+0	1,7E+0	3,0E+0	1,4E+0	5,8E+0	2,4E+0	9,7E-1
CT from soil air to surface-flux	CTsao->ém	(mg/m2/s)/(mg/l)	8,9E-3	8,6E-4	3,5E-3	3,1E-4	1,3E-3	6,6E-4	1,3E-3	6,5E-4	1,4E-3	6,8E-4	7,4E-4	1,8E-3	7,3E-4
CT without / CT with depletion of the source	**CT / CT**	-	**3,3**	**1,01**	**8,5**	**94**	**22**	**1,3**	**23**	**1,3**	**21**	**1,3**	**40**	**17**	**1,2**
CT diffusion only / convection & depletion	CT / CT	%	2,1%	18,3%	5,5%	122,5%	19,9%	16,5%	22,1%	18,0%	18,2%	15,7%	38,1%	21,3%	21,3%
CT retained: Min (convection + diffusion without depletion; convection only with depletion + diffusion only)															
CT from soil air to surface-flux	CTsao->ém	(mg/m2/s)/(mg/l)	9,1E-3	8,7E-4	3,7E-3	7,0E-4	1,6E-3	7,7E-4	1,6E-3	7,7E-4	1,7E-3	7,9E-4	1,0E-3	2,1E-3	8,7E-4

As expected, the impact of the modelled depletion increases with volatility and with the height of the top of the source: over one year, it ranges from 1% for butanol 2.5 m under the slab, up to a factor 94 for vinyl chloride immediately under the slab. In that time, the top of the source descends deeper in the soil, from 3.5 cm up to 14 m deeper respectively (assuming a uniform source layer over this depth, which was not the case at the site). Due to this impact, the diffusive flux (without depletion of the source) becomes often significant (20% or more of the convective flux with depletion of the source).

4. Measure-model comparison on sites

4.1. Site n^{r} 2 - field investigations: site, material and methods

The site N^{r}2 (Figure 1) was an industrial building located in an urban area, contaminated with aromatic hydrocarbons in unsaturated soils. This building had a concrete slab and was surrounded by other buildings, asphalt or concrete roads and bare ground, and grasses.
The characteristics of the building such as its dimensions and the (visual) quality of the floor were registered. The building got demolished and the underlying ground was eventually excavated, which allowed us a better characterization of the soils (lithology, size distribution, etc.).

The field investigations were performed at different seasons (October, December, following June). The meteorological data were collected for each investigation. We could heat the building in winter, allowing conditions more favourable to the convective transfer of vapour (cf. « stack effects »).

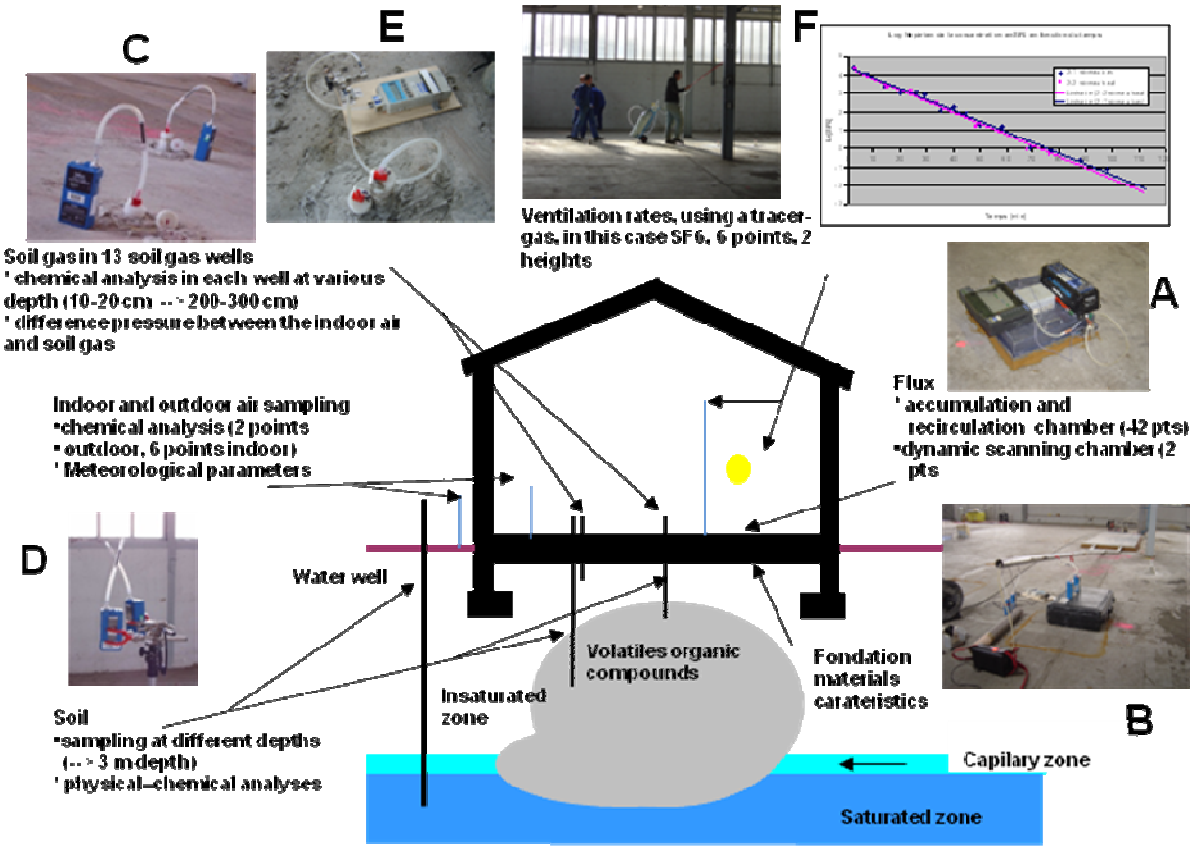

Figure 1 : Field investigations

Flux measurements were realized at the slab surface, using two devices developed by INERIS:

- The « accumulation chamber » [18] (Figure 1-A): gases emitted from the site within an elementary surface (50 cm x 50 cm) are pumped, sent to an analyzer and reinjected into the chamber (H = 20 cm), creating a recirculating flow and then an accumulation in the chamber. The surface flux can be easily derived from the measurement of the atmosphere enrichment as a function of time. The flow of contaminant is expressed relatively to the standard gas chosen [18]. This measurement system is easy and rapid to operate (One measurement every 5 to 10 minutes, but not very precise and rather indicative (FID).
- The “dynamic scanning chamber” [19] displayed in Figure 2-B is a chamber connected to an inert gas supply system and an exit with measurement points. The system gathers contaminant gas emitted from soil within the inert gas flow. The mixed gas sampled is analyzed. Therefore the measured

parameters (concentrations and outgoing air-flows) allow to quantify the flow of emitted vapours outgoing from the chamber, and thus to deduce the flow released through the concrete slab. This approach allows a precise quantification of the various emitted substances. Because of the size of the chamber (L : 250 cm, l :100 cm, H : 15 cm) and the operating time required to reach low quantification limits, only 1 to 3 points can be measured in one day.

About forty measurements of soil-to-air fluxes with the "accumulation chamber" were carried out at one field investigations (October), according to a regular grid (2 m x 4 m).

During the campaigns of October and December, no flux was detected, and this even in the slab zones showing numerous cracks, so that no measure with this chamber was realized afterward but also no indications could be gained on the most suitable positions for the dynamic chamber. The "dynamic chamber" points were located on zones previously identified as polluted by hydrocarbons and presenting a fissured slab (2 points in October and December, only one point in June to be checked following an absence of measurable flux in December).

Soil and slab sampling at different depths and subsequent physical–chemical analyses (organic carbon fraction, size distribution, permeability, concentrations, etc.), Soil samples were analyzed for the organic compounds, like benzene, toluene, ethylbenzene, xylenes and naphthalene.

Based on the data gathered on the lithology and the soil contamination, thirteen soil gas wells were installed at various depths (sampling depth between 0,2-0,4 m and 2-3 m) in the unsaturated zone (source layer and above) in a selected area of the building (Figure 1-C). Soil gas was sampled during the 3 field investigations.

The pressure difference between the indoor air and soil gas was measured in each gas well, using a differential pressure measuring device, with a detection limit and a precision of 1 Pa (Figure 1-E).

Indoor air and outdoor air were sampled respectively at 7 and 2 points (downstream and upstream of the source) during the 3 field investigations, at a height of about 1 m (Figure 1-D), and analysed.

Air exchange rates were characterized using a tracer gas (SF6): after the injection of SF6 in the indoor air at several points and heights (6 points and 2 heights for the big hall, 1 point and 1 height for the office within the big hall), air samples were collected at two heights at different times and analyzed by a chromatograph. The air exchange rate was then calculated using the following formula: $Ln(C/C0) = -x\ (t-t0)$, where C is the tracer-gas concentration at time t, C0 is the tracer gas concentration at time t0, x is the air exchange rate in the buildings (Figure 1-F),

4.2. Site n^r 2 - field investigations: results

Significant soil concentrations of benzene and naphthalene were observed, generally in layers situated below 1,5 m depth, with values respectively in the order of 150 mg / kg and 2200 mg / kg (arithmetic average). Only benzene and naphthalene data are treated in the present paper, due to their volatility and their high concentrations measured in soils.

The measured soil gas and indoor air concentrations for benzene and naphthalene are summarized in the in Table 1:

Benzene mg/m^3	**Oct. 2004**	**Dec. 2004**	**June 2005**
Soil gas (a), arithmetic average	2282 [105-3949]	784 [10-1500]	1614 [nd-2616]
Indoor air, maximum	0,01 [nd-0,01]	0,18 (b) *[nd-0,18]*	0,01 [nd-0,01]
Naphthalene mg/m^3	**Oct. 2004**	**Dec. 2004**	**Juin 2005**
Soil gas (a), arithmetic average	0,4 [0,02-0,9]	0,8 [<QL-1,8]	1,6 [< QL-5,7]
Indoor air, maximum	< 0,001 (LQ) *[nd-<LQ]*	< 0,001 (LQ) *[nd-<LQ]*	0,009 *(b)* [nd-0,009]
(a) : depth: 1,8-3 m ; (b) : same measurement point for max of Benzene in December 2004 and max of Naphthalene in June 2005 ; nd : not detected ; QL : quantification limit of 0,001 mg/m^3 for naphthalene ; *[minimum – maximum]*			

Table 1 : Site n^{r}2 – Summary of soil gas and indoor air concentrations (mg/m^3) for benzene and naphthalene

Those results show significant time and spatial variations in soil gas and indoor air concentrations. This was also observed with surface fluxes.

In a same soil gas well, for example, for naphthalene, the maximal time variation is two orders of magnitude, with a maximal concentration in June. Between different soil gas wells, but at the same time and same sampling depth, concentrations varied within a range of three orders of magnitude (for example benzene in June).
The indoor air concentrations varied within a range of several orders of magnitude over time, for example, for benzene and naphthalene, one order of magnitude between December and June. The indoor air concentrations during the same field investigations were in the same order, with some exception (3 orders of magnitude for benzene in December (maximum concentration)).
In all soil wells and for all campaigns, the indoor air/soil gas pressure difference was in the range of the detection limit of the material (1 Pa), except in December, when the building was heated (2 Pa).
The measured air exchange rates were respectively 0,6, 1,8, 0,8 $hour^{-1}$ in October, December and June.
Except for the higher benzene indoor concentrations in December (in spite of lower soil gas concentrations) possibly related to the heating and the subsequent higher pressure difference, the tremendous variations of concentrations could not be explained with the available data, especially on concentrations, fluxes, building characteristics or meteorological conditions.

4.3. Modeling

A steady-state modelling of the indoor air concentrations was based on the analytical equations of Johnson & Ettinger [4] and VOLASOIL [8] adapted by INERIS [10] (multi-layer model, named "VOLASOIL-a").
The main input data are reported in Table 2. The majority of those values were measured at the site. Some data estimated from expert judgment, modeling and/or literature [4 ; 8] were also used. For example, the concrete slab was parameterized separately according to each model, based on our understanding of the mechanisms at stake in each model and on literature data.

	Value	**Origin of the data**
Soil	Sand, sand with silt and gravel	
Organic carbon fraction	0,5	Measured
Dry bulk density (kg/dm^3)	1,7	Estimated from standard values of similar soils, with filling of gravel gaps by sand and consistency with measured water content
Total porosity	0,25	
Water-filled porosity	0,19	
Air-filled porosity	0,06	
Gas conductivity (m^2)	$1\ 10^{-13}$	Estimated from measured water permeability (~ 10^{-6} m/s) and standard values for similar soil; ~ 6.10^{-9} m^3/m/Pa/s
Building		
Length, width, height (m)		Measured
Floor thickness (m)		Average measured
Fraction of openings (VOLASOIL)	0,00001	VOLASOIL standard value, wet slab "medium" quality [8]
Slab air permeability (m^3/m/Pa/s, VOLASOIL)	$1,1.10^{-6}$	
Crack width in the slab (cm, J&E)	0,1	Standard values of J&E [4]
Fraction of cracks (J&E)		Estimated from J&E standards [4] and real building
Air exchange rate (h^{-1})	0,6 ; 1,8 ; 0,8	Measured, campaign specific
Pressure difference between the indoor air and the soil gas (Pa)	1 or 2	Measured, campaign specific
Source layer		
Depth (m)	1,8	
Soil concentrations		Arithmetic average of the concentrations measured in soil between 2 and 3 m
Soil gas concentrations	See Table 1	For each campaign, arithmetic average of the concentrations measured in soil gas between 1,8 and 3 m
Indoor air concentrations	See Table 1	For each campaign, maximum concentrations or quantification limit (when not quantified).

Table 2 : Values of the main modeling parameters

4.4. Comparison of predicted and observed indoor air concentrations

With both models, the modelling of indoor air concentrations were performed starting from soil concentrations and from soil gas concentrations.

The comparisons were not limited to the concentrations in the indoor air, but also concerned intermediate data such as soil gas and vapour fluxes.
Figure 2 plots measured and predicted indoor air values for benzene and naphthalene in the « soil source » case, regarding predicted/observed ratio for site n^{r} 2.
The results of the modeling from a soil gas source for the December campaign for benzene and the June campaign for the naphthalene are not illustrated in this document but only commented later in a general way.
For comparison, some results of the study of the site n^{r}1 for trichlorethene [16] are also plotted.

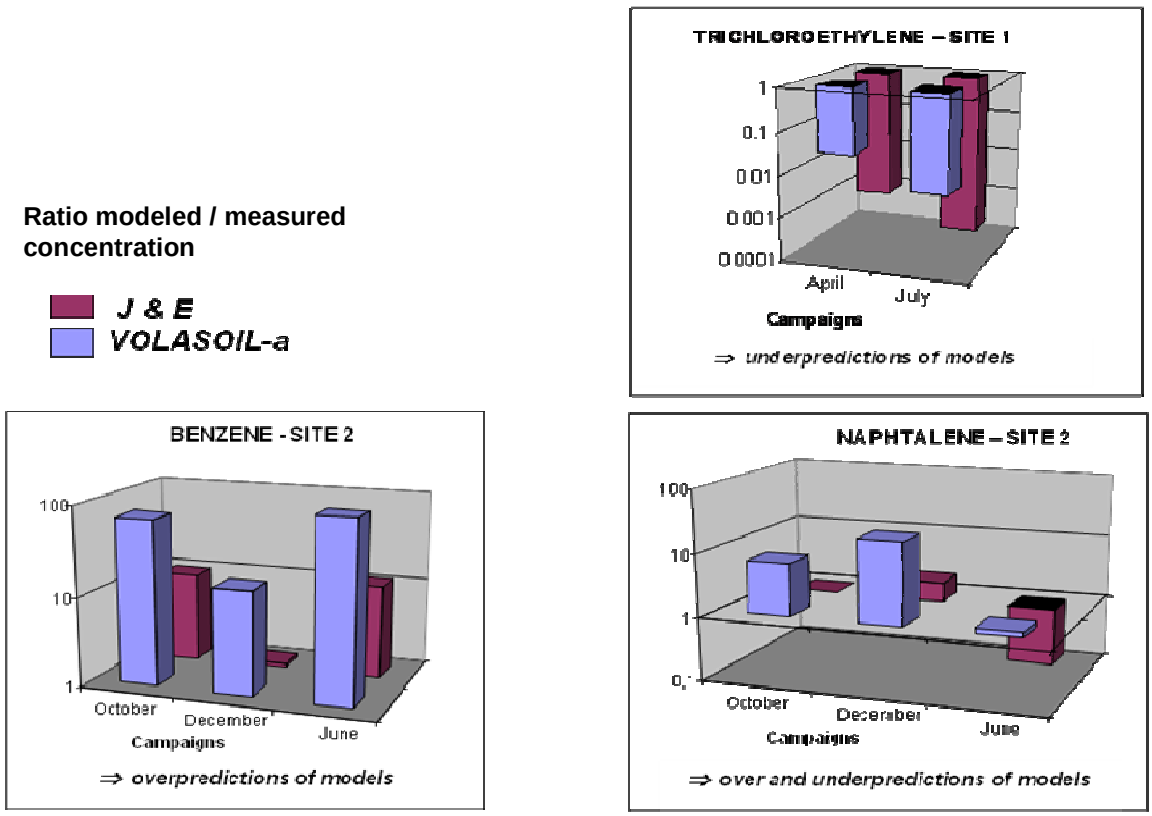

Figure 2: Comparison of modelled and measured indoor air concentrations (starting from soil concentrations)

The results of those simulations lead to the following comments:

- Modelled soil gas concentrations (triphase equilibrium starting from soil concentrations) differed significantly from measured soil gas concentrations, up to several orders of magnitude depending on the choice of input values of the models and on the field campaign;
- For the « VOLASOIL-a » modeling : starting from soil concentrations, the predictions were conservative by up to one order of magnitude for benzene and naphthalene. The lowest overestimation was observed in December (with heating and measurable pressure difference) for benzene and in June for naphthalene. Starting from soil gas concentrations, the predicted indoor air concentrations are in the same order of magnitude as the measured concentrations for benzene (December), much lower (several orders of magnitudes) for naphthalene (June);
- For the « J & E » modeling : starting from soil concentrations, the predictions also tend to be overconservative, globally with an order of magnitude (with an exception). In the case of naphthalene, in June the concentration predicted in indoor air is underconservative by an order of magnitude

(campaign with the highest measured indoor air concentrations). Starting from soil gas concentrations, the model predictions underestimated the indoor air concentrations by several orders of magnitude.

- On site n°1 [16], the modeling for trichlorethene and perchlorethene, underestimated the observed concentrations, with one to four order of magnitude (starting from soil and soil gas concentrations). But on this site, there were not so many points of measures, and indoor concentrations were close to quantification limits.

4.5. Sensitivity and uncertainty analysis – Parametric study

A sensitivity and uncertainty analysis was realized. Various –including significant- impacts could be obtained by modifying the parameter values within their respective possible ranges, in spite of an extensive site characterisation. The most sensitive and uncertain parameters were certain physico-chemical parameters of soil and building characteristics. But they strongly depend on the model, which can be related to the model conceptualization. Uncertainties on such parameters as soil gas porosity, soil gas permeability, pressure difference between the indoor air and the soil gas, impacted the modelled concentrations with up to an order of magnitude.
Several reasons can be considered to explain the variations between observed and modeling data, connected either to the input parameters of the models, among others the results of the field investigations and their uncertainties, or to the specific conceptualization of the transfer phenomena of each model. But no trend could be outlined according to the model, the typology of the site or the characteristics of studied substances.

As an example: the measured pressure differences between the indoor air and the soil gas varied between the investigation campaigns: 2 Pa in December, otherwise measured at 1 Pa (detection limit and precision of the device). The impact of this parameter is minor in the VOLASOIL-a modelling: diffusion is the main transfer mechanism in this modeling, due to the low gas permeability of the soil (and to the depth of the source under the slab; the slab is 130 times more permeable)[3]. But the impact of the same parameter is major with "J*E" (allowed by a permeable slab and a different representation of the diffusive soil air flux). For example, for naphthalene, if we choose 0.1 Pa instead of 1 Pa, the indoor air concentration modelled with "J*E" decreases by a factor 10 about.

5. Conclusion and recommendation

The modeling of a depleting source led to downsizing the vapour flux by one order of magnitude or more over one year in the experimental site. This illustrates the importance of this modeling. The mathematical developments of VOLASOIL presented here should allow a broader use of VOLASOIL, especially for a source next to the concrete slab.
The comparisons between predicted and measured concentrations in indoor air showed on the real site over-prediction by the models and in some cases under-predictions by the models with one or two orders of magnitude. In spite of an extensive site characterisation, those differences, and the significant time and space variability in measured soil gas or indoor air concentrations could often not be explained. Significant impacts on the modelled concentrations could be obtained by modifying the parameter values within their respective possible ranges.

The study emphasizes the importance of a humble attitude towards the results of the modeling of vapour transfer, in the current state of model validation. Combining models and measurements is essential for a “robust” risk assessment. A comprehensive understanding of the model used, its concept and its equations, is essential. We recommend to re-code one’s own tools so as to better test and understand the sensitivity of the model in different situations.
Improvements in modeling and measuring vapour intrusion are still possible. When dealing with finite source modelling, the research should be extended to the impact of degradation in the vadose zone for benzene and e.g vinyl chloride as a source of variability and systematic differences.
Detailed quantitative measurements and interpretation of the main site parameters appear essential when aiming at model verification. This is a difficult and time-consuming work, which has to be repeated with

[3] On the contrary the soil considered for the modelling of the depleting source has permeability 100 times higher, allowing the convection to predominate over the diffusion (even for a deep source).

different types of sites (building designs, construction materials, soil) and at different periods under adequate conditions (heating, “normal” ventilation…). Collaborations are needed, at national and international scales, so as to gather strengths on data collection and interpretation. Such collaborations are initiated for example with the HERACLES initiative and with the French and European research projects FLUXOBAT and CITYCHLOR about chlorinated solvents pollution in soil and groundwater.

6. Acknowledgements

This work is part of a research-project financially supported by the French Ministry in charge of the Environment and by the French public Agency ADEME. We are also grateful to the site owners for their collaboration. The opinions expressed in this paper are those of the authors and do not necessary represent those of the funding organizations.
We thank Frank Swartjes and Johannes Lizjen, from RIVM, for the long term cooperation on this topic, and Johannes Lizjen for his valuable review of this paper.

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